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CHEMISTRY

1965

SovietRxiv

Abstract

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UDC 546.186.162 + 547.224

CHEMISTRY

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STABLE SALTS OF ALKOXYAMINOPHOSPHONIUMS WITH A DELOCALIZED ONIUM CHARGE

As is known, the cations of alkoxyphosphonium salts containing the grouping $[\equiv\overset{+}{\mathrm{P}}-\mathrm{OR}]X^-$ are unstable substances, readily splitting off an alkyl cation, usually in the form of an alkyl halide. Such are the intermediate products of the Arbuzov rearrangement ([1,2]) of trialkyl phosphites (I) or esters of phosphinous acids (II) and (III), the intermediate products of the Menshutkin–Wichelhaus reaction ([3,4]) (IV), enolphosphonium salts ([5–7]) (V), and a number of others.

$$[(\mathrm{RO})_3\overset{+}{\mathrm{P}}\mathrm{R}']X^-; \qquad [\mathrm{R}_2\overset{+}{\mathrm{P}}(\mathrm{OR})_2]X^-; \qquad [\mathrm{R}_3\overset{+}{\mathrm{P}}\mathrm{OR}]X^-;$$

(I) (II) (III)

$$[(\mathrm{RO})_3\overset{+}{\mathrm{P}}X]X^-; \qquad \left[\mathrm{Ph}_3\overset{+}{\mathrm{P}}-\mathrm{O}-\mathrm{C}=\mathrm{C}\langle\right]X^-.$$

(IV) (V)

Most compounds of this type decompose already at room temperature, although some of them have been identified ([8,9]). More stable in the form of fluoroborates ([10]), these compounds nevertheless decompose readily. Several stable alkoxyaminophosphonium salts ([11]) have been described, containing two (VI) or even one amino group (VII). However, salts with one amino group are only slightly stable. Thus, two of us ([12]) showed that O,O-dialkyl-N-phenylamidophosphites

$$[(\mathrm{R}_2\mathrm{N})_2\overset{+}{\mathrm{P}}(\mathrm{OR}')\mathrm{CH}_3]\mathrm{J}^-; \qquad [\mathrm{R}_2\mathrm{N}\overset{+}{\mathrm{P}}(\mathrm{OR}')_2\mathrm{CH}_3]\mathrm{J}^-$$

(VI) (VII)

(VIII), on interaction with methyl iodide, undergo the Arbuzov rearrangement at the ester part of the molecule:

$$(RO)_2PNHPh \xrightarrow{CH_3J} [(RO)_2\overset{+}{P}(NHPh)CH_3]J^- \xrightarrow[-RJ]{} RO\Big\backslash P\left(\begin{matrix}NHPh\\ CH_3\end{matrix}\right)$$

(VIII)

Intermediate alkoxyphosphonium salts are not detected in this case. Similar results were obtained by A. I. Razumov (13).

Apparently, the stability of alkoxyaminophosphonium cations is associated with delocalization of the onium charge, for example:

$$>N-\overset{OR}{\overset{+}{P}}-N< \;\longleftrightarrow\; >\overset{+}{N}=\overset{OR}{P}-N< \;\longleftrightarrow\; >N-\overset{OR}{P}=\overset{+}{N}<$$

with the use of the *d*-levels of the phosphorus atom. The possibility of such delocalization has been discussed in the literature (14). If this proposition is correct, then increasing the delocalization of the onium charge in the phosphonium cation should increase the stability of such salts. Experiment confirmed this assumption.

We obtained a stable phosphonium salt with two alkoxy groups at the phosphorus atom in the reaction of O,O-diethyl-(1-ethyl-2-pyridoni-

···imido) phosphite (15) (IX) with an equimolar amount of methyl iodide in petroleum ether at room temperature. The structure of the methyl iodide adduct of diethoxy-(1-ethyl-2-pyridonimino)-phosphonium (X) is proved as follows:

$$(IX) \xrightarrow{CH_3J} (X)\,J^- \xrightarrow{NaBF_4} (XI)\,BF_4^-$$

$$CH_3P(OC_2H_5)_2\ (XII)\ +\ (XIII)\,BF_4^- \longrightarrow (XI)$$

This substance contains no trivalent phosphorus, since after hydrolysis it does not reduce sublimate to calomel. According to Zeisel, two alkoxyl groups are determined in it (found, %: C_2H_5O 23.2, 23.5; calculated 23.5). The iodine atom in it is ionically bound, since it is capable of being exchanged for a BF_4 group under the action of sodium borofluoride. The methyl diethoxy-(1-ethyl-2-pyridonimino)-phosphonium borofluoride (XI) formed in this process was also obtained by us by a counter-synthesis—the reaction of *O*, *O*-diethyl methylphosphinite (XII) (16) with 2-azido-1-ethylpyridinium borofluoride (XIII) (17). The preparations obtained by the two routes had the same melting point in a simple and mixed sample.

The stability of substances of this type is undoubtedly connected with delocalization of the positive charge in the cation between the phosphorus atom and two nitrogen atoms:

$$> \mathrm{N{-}N{=}P^+{-}CH_3} \leftrightarrow > \mathrm{N^+{=}N{=}P{-}CH_3} \leftrightarrow > \mathrm{N^+{-}N{=}P{-}CH_3}$$

A similar structure with a delocalized onium charge is possessed by hydrogen borofluoride *O*, *O*, *O*-triethyl-(3-ethyl-2-benzothiazoliniylimino)-phosphate (XIV), which we recently obtained by the interaction of 2-azido-3-ethylbenzothiazolinium borofluoride with triethyl phosphite (15):

$$\text{2-azido-3-ethylbenzothiazolinium } BF_4^- + P(OC_2H_5)_3 \longrightarrow$$

$$[\text{3-ethylbenzothiazolinium-2-ylimino-}P(OC_2H_5)_3 \leftrightarrow \text{3-ethylbenzothiazolinylideneimino-}P^+(OC_2H_5)_3]\,BF_4^-$$

This is a very stable alkoxyphosphonium salt with three alkoxyl groups at phosphorus. Unlike other compounds with a P–N bond, it does not react with carbon disulfide (even on boiling for 6 hours). However, conversion of the phosphonium salt into the hydroxide leads to typical onium decomposition. Thus, under the action of caustic soda in an aqueous-alcoholic medium on hydrogen borofluoride *O*, *O*, *O*-triethyl-(3-ethylbenzothiazoliniylimido)-phosphate (XIV) at room temperature there is formed

O,O-diethyl (3-ethyl-2-benzothiazolonimido)phosphate (XV). The same substance was obtained by us by an independent method from diethyl chlorophosphate and 3-ethyl-2-benzothiazolonimine (^{18}):

$$\text{(XIV)} \xrightarrow{\text{NaOH}} \text{O,O-diethyl (3-ethyl-2-benzothiazolonimido)phosphate (XV)}$$
$$\leftarrow \text{3-ethyl-2-benzothiazolonimine} + ClP(O)(OC_2H_5)_2$$

Both preparations are thick, viscous liquids; they have coincident IR spectra and, on thin-layer chromatography on silica gel (solvent hexane–acetone 1:1, KSK-grade silica gel containing 6% water), show identical R_f values (0.74).

Table 1

Nos.	Yield, %	$T_{dec.}$, °C	Empirical formula	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	F, % found	F, % calculated	N, % found	N, % calculated
X[1]	48	86.5–87	$C_{12}H_{22}N_2IPO_2$	37.7 37.3	37.5	5.8 5.7	5.8	7.7 7.8	8.1	–	–	–	–
XI[2]	56	85–86	$C_{12}H_{22}N_2PO_2 \cdot BF_4$	42.3 42.4	41.9	6.5 6.4	6.4	9.1	9.0	22.3	22.1	–	–

Nos.	Yield, %	$T_{dec.}$, °C	Empirical formula	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	F, % found	F, % calculated	N, % found	N, % calculated
XI[3]	11	85–86	$C_{12}H_{22}N_2PO_2BF_4$	41.4 41.3	41.9	6.3 6.4	6.4	8.8 8.9	9.0	22.7	22.1	–	–
XV[4]	100	–	$C_{13}H_{19}N_2PSO_3$	50.0 49.8	49.7	6.0 6.1	6.1	9.6 9.6	9.8	–	–	8.8 8.7	8.9
XV[5]	27	–	$C_{13}H_{19}N_2PSO_3$	49.2 49.0	49.7	6.1 6.2	6.1	10.0 10.0	9.8	–	–	8.6 8.9	8.9
XVI	43	159–160	$C_{18}H_{28}N_4PO_2BF_4$	48.2 48.5	48.0	6.1 6.2	6.3	7.2 7.2	6.9	17.0 16.7	16.9	12.6 12.3	12.5
XVII	68	94–95[6]	$C_{18}H_{28}N_6PO_2BF_4$	45.4 45.5	45.2	5.9 5.8	5.9	7.1 6.8	6.5	15.9 16.5	15.9	17.6 17.7	17.6

[1] Found %: J 33.0, 32.8; calculated %: J 33.0. [2] Starting from iodomethylate (X). [3] Starting from azide (XIII). [4] Starting from imidophosphate (XIV), n_D^{20} 1.5790. [5] Starting from 3-ethyl-2-benzothiazolonimine; b.p. 180–200° (bath temperature) (10^{-4} mm); n_D^{20} 1.5792. [6] Decomposition temperature.

An even greater stability toward the action of high temperature and various reagents is exhibited by the phosphazacyanines, the first representative of which we recently described ([15]).

Thus, the symmetrical pyridine phosphazacyanine (XVI), obtained according to the scheme below,*

$$\text{(IX)} + \text{(XIII)} \longrightarrow \left[\ \text{2-pyridylimino-P(OC}_2\text{H}_5)_2\text{-azimino-1-ethylpyridinium}\ \right]\text{BF}_4^- \xrightarrow{100^\circ}$$

$$\longrightarrow \left[\ \text{bis(1-ethyl-2-pyridylimino)ethyl phosphazacyanine}\ \right]\text{BF}_4^-\ \text{(XVI)} \xrightarrow{\text{HCl}} \text{1-ethyl-2-iminopyri}$$

$$\text{(XVII)} \longrightarrow \text{(XVI)}$$

* Triazene (XVII), formed upon addition of 2-azido-1-ethylpyridinium fluoroborate (XIII) to O,O-diethyl (1-ethyl-2-pyridonimido)phosphite (IX) in dichloroethane at room temperature, can be isolated in pure form and consists of yellow crystals. On heating triazene (XVII) to 100–110°, nitrogen is evolved and phosphazacyanine (XVI) is formed, which can also be obtained without isolating the triazene in pure form. The fluoroborate anion in phosphazacyanines can readily be replaced by the tetraphenylboron anion.

it is not changed either by aqueous alcoholic alkali or by heating to 100° for 1.5 h with an excess of 40% aqueous sodium hydroxide. On boiling with concentrated HCl for 3 h, its hydrolysis occurs with formation of 1-ethyl-2-pyridonimine, which was isolated by the action of alkali and identified by gas-liquid chromatography.

The high stability of phosphazacyanine (XVI) is undoubtedly due to the delocalization of the onium charge, typical of polymethine cyanines—in our case between the phosphorus atom and four nitrogen atoms. Thus, the distribution of the onium charge extends over both pyridine rings attached to phosphorus. Hence it may be asserted that the tetrahedral phosphorus atom, included in the middle of the conjugation chain, does not prevent its formation, i.e., is not a barrier interrupting conjugation. However, like the unsymmetrical phosphazacyanine described by us earlier, with one pyridine and one benzothiazole nucleus (15), phosphazacyanine (XVI) is colorless (absorption maxima in the UV spectrum in alcohol are at 225 and 330 mμ), which makes it possible to assign the conjugation in its molecule to the type of weak (low-frequency) conjugations. The constants and yields of the substances are given in Table 1.

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Received
25 V 1965

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